Interface Stability During Rapid Directional Solidification

INTERFACE STABILITY DURING RAPID DIRECTIONAL SOLIDIFICATION

David E. Hoglund and Michael J. Aziz
Division of Applied Sciences, Harvard University, Cambridge, MA 02138

ABSTRACT

At the solidification velocities observed during pulsed laser annealing, the planar interface between solid and liquid is stabilized by capillarity and nonequilibrium effects such as solute trapping. We used Rutherford backscattering and electron microscopy to determine the nonequilibrium partition coefficient and critical concentration for breakdown of the planar interface as a function of interface velocity for Sn-implanted silicon. This allows us to test the applicability of the Mullins-Sekerka stability theory to interfaces not in local equilibrium and to test the Coriell-Sekerka and other theories for oscillatory instabilities.

INTRODUCTION

During steady-state solidification of a single-component melt, a planar solid-liquid interface will remain stable as long as heat is removed through the solid. If the interface is in local equilibrium, then the solid stays below the melting temperature, the interface at the melting temperature, and the liquid above the melting temperature. Since the liquid is not undercooled, the interface is stable.

The stability criterion for a two-component melt is more complicated. Tiller *et al.* [1] analyzed the effect of solute preferentially partitioning into the liquid. They showed that for any straight-line liquidus, there exists a critical concentration of solute in the bulk liquid such that the interface is unstable. Solute rejected by the interface creates a concentration gradient in the liquid layer next to the interface. The concentration gradient causes the liquid ahead of the interface to be undercooled with regard to the composition-dependent liquidus temperature despite being at a higher temperature than the interface. This is the basis of the constitutional supercooling condition.

Later, Mullins and Sekerka [2] used linear perturbation analysis to evaluate interface stability. They started their analysis with an unperturbed planar interface in local equilibrium moving at constant velocity. Then they calculated the time dependence of the amplitude of an infinitesimal sinusoidal perturbation imposed on the interface. Since the perturbation curves the interface, they took capillarity into account and found that it had a stabilizing effect, especially at high solidification velocities. The effect is strong enough that for any concentration of solute in the bulk liquid, the interface is stable if the velocity is high enough. A high velocity allows little time for lateral diffusion of solute, so no large scale perturbations can form. Small scale perturbations do have time to form, but these are the perturbations that capillarity resists most strongly. This is the basis for the Mullins-Sekerka absolute stability limit. For high velocities, the absolute stability limit reduces to the following simple form:

$$C_\infty = \frac{k^2 T_M \Gamma v}{(k-1)\, m\, D_L} \qquad (1)$$

where C_∞ is the critical bulk concentration in the liquid to cause interface breakdown, k is the partition coefficient (ratio of the solute concentration in the growing solid to that in the liquid at the interface), T_M is the melting point of pure solvent, Γ is the capillarity constant (ratio of surface tension to heat of fusion), v is the interface velocity, m is the slope of the straight-line liquidus, and D_L is the diffusivity of solute in the bulk of the liquid.

The Mullins-Sekerka analysis assumes local equilibrium at the the interface. This assumption is least likely to hold at velocities where equation (1) is most likely to be valid. The limit of interface stability should be sensitive to nonequilibrium effects because the suppressed partitioning [3] or "solute trapping" associated with nonequilibrium solidification ought to stabilize the interface.

Mat. Res. Soc. Symp. Proc. Vol. 205. ©1992 Materials Research Society

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Early tests of interface stability under nonequilibrium conditions [4-6] showed that stabilization did indeed occur. Now that the kinetic undercooling function in pure silicon [7-9] and solute trapping function for various dopants in silicon [10-12] have been measured, it is possible to incorporate nonequilibrium effects systematically into stability theory.

Aziz and Kaplan [13] have proposed a model for the interface response functions called the "continuous growth model without solute drag." For solute trapping in the dilute solution regime, the model gives

$$k(v) = \frac{(v/v_D) + k_e}{(v/v_D) + 1} \qquad (2)$$

where k is the nonequilibrium partition coefficient, k_e is the equilibrium partition coefficient, v the interface velocity, and v_D the diffusive velocity. Using the continuous growth model and assuming a dilute solution, a straight-line equilibrium liquidus and solidus, and a solidification velocity much less than the maximum solidification velocity at infinite driving force, Boettinger has derived a simple expression [14] for the slope of the kinetic liquidus,

$$m(k(v)) = m_e \times \left\{ 1 + \frac{k_e - k\left(1 - \ln\frac{k}{k_e}\right)}{1 - k_e} \right\} , \qquad (3)$$

where k is the nonequilibrium partition coefficient, k_e is the equilibrium partition coefficient, and m_e is the slope of the equilibrium liquidus. Substituting the partition coefficient of equation (2) and the liquidus slope of equation (3) into the Mullins-Sekerka result (not just equation (1), but the full solution) yields a thermodynamically consistent formulation of nonequilibrium linear stability theory.

We recently reported [15] the first quantitative test of stability theory, using Sn-implanted Si-on-sapphire (SOS) samples. However, the large number of extended defects in these samples not only made identification of the cell walls difficult but also might have influenced the breakdown of the planar interface. Here we report similar measurements performed on bulk single crystal Si(100). We compare our measurements of the onset of instability to the theory. Since the key parameters in the theory have already been measured, this constitutes a quantitative test with no free parameters.

EXPERIMENT

Wafers of (100) silicon were implanted with 165 keV $^{120}Sn^+$ at doses of 1 and $2\times10^{16}/cm^2$. Samples were melted with a 30ns FWHM XeCl (308nm) excimer laser pulse. Preheating samples with a 80W CO_2 laser just before firing the excimer laser allowed us to control the thermal conductivity and thermal gradient in the material and thereby extend the range of solidification velocities to lower velocities. Surface melt durations were measured using the transient reflectivity of a low power Ar ion laser. Since for our samples the melt duration as a function of laser fluence was close to that of pure bulk silicon, we could use well calibrated heat flow-simulations of pulsed laser melting of pure silicon [16] to obtain melt depths and solidification velocities for our samples.

After solidification, the Sn concentration-depth profile was measured using Rutherford Backscattering Spectrometry (RBS). Since nonsubstitutionality of dopants has been correlated with interface breakdown [17], we also performed ion channeling analysis. Figure 1 shows data for one sample. We initially assumed that the interface broke down at the depth where the concentration of nonsubstitutional Sn became appreciable. The total concentration of Sn at that depth was taken to be the critical concentration for breakdown. This is exact for steady state solidification. For example, the interpretation of Figure 1 is that the interface was stable from 3300Å (the maximum melt depth) to 1500Å, but then broke down. The critical concentration for breakdown is the total Sn concentration at 1500Å, about 0.7 atomic percent Sn.

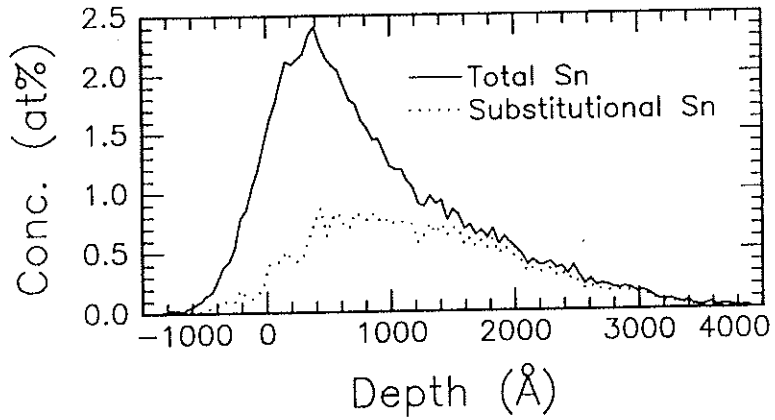

Figure 1: RBS /channeling data for Sn-implanted bulk Si(100) after pulsed laser melting.

DISCUSSION

Figure 2 shows our data. It also shows a full numerical solution to the Mullins-Sekerka theory rather than the high velocity limit of equation (1). For the dashed curve, we assumed that k and m had their equilibrium values. For the solid curve, we used the k of equation (2) and the m of equation (3). The equilibrium partition coefficient is $k_e = 0.016$. The diffusive velocity, $v_D = 17$ m/s, and the liquid diffusivity, $D_L = 2.5\times10^{-4}$ cm^2/sec, were taken from solute trapping experiments [15]. Values of other thermophysical parameters not taken from Cahn, Coriell, and Boettinger [18] are: capillarity factor $T_M\Gamma = 1.3\times10^{-7}$ Km obtained from homogeneous nucleation experiments [19]; and slope of the equilibrium liquidus $m_e = -460$ K [20]. The temperature gradient in the liquid was estimated to be 2×10^4 K/m from heat flow calculations. The temperature gradient in the solid was approximated by the product of the velocity and the latent heat divided by the thermal conductivity in the solid. Although these estimates are reliable, the predictions are highly insensitive to the thermal gradients for solidification velocities in the range that we are investigating.

Theory and experiment agree quite well considering that there are no adjustable parameters in the comparison. Also, the new data points agree with the previously reported results for silicon-on-sapphire samples [15]. Three ways of refining this work are in progress. The cell size, measured in plan-view transmission electron microscopy (TEM), can be compared with theory. Cross-section TEM is under way to verify that the interface did break down at the position inferred by RBS/channeling. Finally, we should consider that there might be a delay in this non-steady-state experiment between the onset of instability and the appearance of nonsubstitutional impurities (note that all of our data lie slightly above the curve predicted by the theory). Both the second and third items mentioned above would tend to cause us to over-estimate the critical concentration. Also, it is possible that the surface tension, taken from nucleation experiments, might turn out to be too low due to heterogeneous nucleation. In this case the theoretical curve in Fig. 2 would be moved upwards as equation (1) shows.

We have also considered theories for oscillatory instabilities such those developed by Coriell and Sekerka [21] and Merchant and Davis [22]. It now seems that Si(Sn) is not a good system for studying oscillatory instabilities because the crystal/melt interface is too sluggish. According to calculations for the onset of instabilities [23, 24], in our present experiments the interfaces should always become susceptible to steady instabilities before oscillating ones.

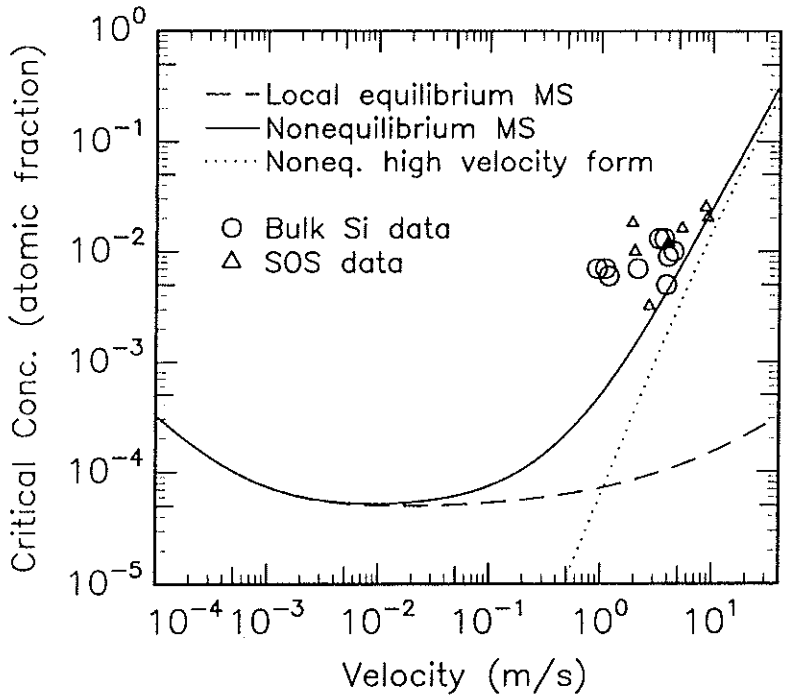

Figure 2: Critical concentration above which cellular breakdown of planar interface occurs. Curves: (- - -) Mullins-Sekerka theory assuming local equilibrium; (——) Mullins-Sekerka theory assuming k(v) and m(k(v)) given by equations (2) and (3); (·····) Equation (1), simplified form of the Mullins-Sekerka theory valid at high velocities, assuming k(v) and m(k(v)) given by equations (2) and (3).

ACKNOWLEDGEMENTS

We are grateful to J.Y. Tsao, P.S. Peercy, S.R. Stiffler and M.O. Thompson for collaboration, and to C. Hayzelden for instruction in microscopy, in the SOS study. We thank S.R. Coriell for assistance with the numerical solution to the stability equations. Samples were implanted at the Surface Modification and Characterization Facility at Oak Ridge National Laboratory. Work at Harvard was supported by the DOE through DE-FG02-89ER45401 (J.B. Darby).

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